A Novel Mercury–Palladium Cluster Derived from Metallic Mercury

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Received July 22, 1982

Recently we have reported synthesis [1], structure [2] and reactivity to some organomercurials [3] of several alkylphosphine carbonyl Pd(0) complexes. The reaction with RHgX follows a general pattern [4], common for mononuclear Pd(0) and Pt(0) complexes, that is the insertion of PdL or Pd(CO)L moiety occurs. However, the reaction between cluster $Pd_4(CO)_5(PEt_3)_4$, *I*, and 8 (α-bromomercuriethyl)-quinoline (for preparation, see [5]) followed the novel route to give an unexpected product, a mixed mercury–palladium cluster $Pd_4(CO)_4(PEt_3)_4(HgBr)_2$ whose structure has been established by X-ray methods [6].

We wish now to report synthesis of another mercury–palladium cluster *II*. The shaking of benzene or heptane solution of cluster *I* with metallic mercury under CO gives rise, after several minutes, to the initial red-violet colour turning dark-green. The dark violet-green rhombic crystals of *II* can be isolated and are quite soluble in benzene, but much less so in heptane. Analytical data for the 5 elements turned out to be in excellent agreement with the formula $Hg[Pd_3(CO)_3(PEt_3)_3]_2$. Molecular weight (determined cryoscopically in benzene) exhibited the tendency to decrease with time, probably indicating an exchange process. The presence of only two carbonyl stretchings, 1862 and 1822 cm^{-1}, reflects the high symmetry of the molecule and the magnitude of ν_{CO} is rather characteristic of semi-bridging $4e^-$ carbonyl ligands [7]. For comparison one can mention 1997 and 1855 cm^{-1} in the former Hg–Pd cluster with non-bridging carbonyls [6]. To summarize, one can assign the structure with two Pd_3 moieties forming a sandwich around the Hg atom that fits the topology of the centered trigonal prism [1] or antiprism [b] (Fig. 1). The high-symmetry structure proposed is supported by the NMR ^{31}P spectrum wherein two singlets are observed at –70 °C in toluene, δ 47.37 and 13.25 ppm. The latter seems to correspond to the starting cluster *I* for which δ 13.14 was found under the same conditions. The presence of this signal in the spectrum of the solution prepared from pure *II* is likely to indicate the following equilibrium:

$$\underset{I}{3Pd_4(CO)_5(PR_3)_4} + 2Hg \rightleftharpoons \underset{II}{2Hg[Pd_3(CO)_3(PR_3)_3]_2} + 3CO$$

This dynamic behaviour can explain why neither satellites due to ^{199}Hg in ^{31}P spectrum, nor direct signals from ^{199}Hg nuclei, were observed. Taking product *II* out of solution as precipitate or removing CO one can shift the equilibrium to the right. The separation of free metal goes much slower.

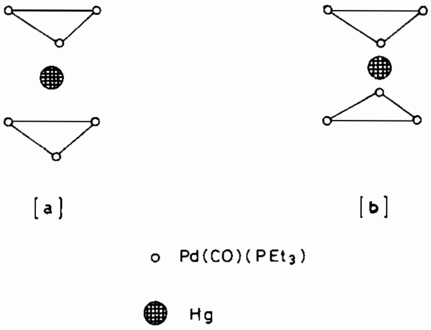

Fig. 1. Proposed structure for the mercury-palladium cluster.

During the formation of *II* from *I* Pd_4 the 'butterfly' loses one metal atom. The structural lability in this family of Pd clusters has been already noted [8]. It is noteworthy that related clusters $Pd_{10}(CO)_{12}(PR_3)_6$, $Pd_3(CO)_3(PPh_3)_4$, $Pd_4(CO)_5(PPh_3)_4$ undergo complete degradation to metals when reacted with metallic mercury. It is remarkable that the triphenylphosphine analogue cannot afford the similar Hg–Pd cluster, which possibly does not exist. The only difference between PEt_3 and PPh_3 is that the former is a much stronger electron donor. Hence we are forced to admit that $Pd_3(CO)_3(PR_3)_3$ should exhibit electron-releasing character as a ligand at mercury atom. The general reason for the stability of seven-atom cluster should probably be sought in the decreasing number of vacant CVMO [9, 10].

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0020-1693/83/0000-0000/$03.00

Experimental

Reaction of $Pd_4(CO)_5(PEt_3)_4$ Cluster, I, *with Mercury*

Solution of *I* (0.90 g) in heptane (35 ml) was shaken in the CO atmosphere with metallic mercury (24 g) for 3 hrs. The green solution was poured out through the paper filter and the solid residue was treated with benzene (20 ml). The benzene solution was filtered to remove metals, added to the heptane fraction and reduced *in vacuo* to 5 ml volume. The dark violet-green crystals were washed with cold heptane and dried *in vacuo.* The yield was 0.59 g (59% of *II* according to the equation abovementioned), dec. 125 °C. *Anal.* Found: C, 28.96; H, 5.28; Hg, 11.9; P, 10.83; Pd, 37.22; CO, 10.1%. Calcd. for $C_{42}H_{90}HgO_6P_6Pd_6$: C, 29.40; H, 5.28; Hg, 11.7; P, 10.83; Pd, 37.20; CO, 9.8%. IR (nujol): 1962, 1822 cm^{-1}. Molecular weight (cryoscopically in benzene): 1860 (after 10 min), 1480 (20 min), 1280 (30 min), calcd.: 1717.

Acknowledgement

We thank Prof. L. M. Venanzi (E.T.H., Zürich) for the communication prior to publication that a phosphinecarbonyl Pt(0) cluster is capable of reacting with metallic mercury.

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